

Final Report

**Central California Ozone Study - Volatile Organic Compounds Collection
and Analysis by the Continuous GC/MS Method.
Data Validation**

Prepared for

San Joaquin Valley Air Pollution Study Agency
C/o
State of California Air Resources Board

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1. INTRODUCTION

Two analytical methods measuring hydrocarbons were conducted in the Central California Ozone Study (CCOS) during the summer of 2000 to examine the affect of emissions on ozone concentration in non-attainment areas in central California (San Francisco Bay Area, Sacramento Valley, and San Joaquin Valley) (Fujita et al., 2000).

1. A continuous Gas Chromatograph/Mass Spectrometer (GC/MS) system composed of an Entech real-time integrator with an Entech 7100 preconcentrator and a Varian 3800 gas chromatograph with a flame ionization detector (FID) and column switching valve interfaced to a Varian Saturn 2000 ion trap mass spectrometer was used for sample collection and analysis. The samples were collected with 1-hour resolution during intensive operational periods (IOP) and 3-hour resolution during the remaining days of the two-month study period or non-intensive operational periods (non-IOP). For this study the continuous GC/MS systems were calibrated for 126 organic compounds including hydrocarbons from C₂ to C₁₂, oxygenated hydrocarbons, and halogenated compounds. C₂ and C₃ hydrocarbons were quantified using a FID detector and the remaining compounds were identified and quantified by MS (Ion Trap) detector.
2. Canister samples collected with 3-hour resolution (0000, 0600, 1300, 1700 and 2100) were analyzed for C₂-C₁₂ hydrocarbons by a Hewlett Packard Gas Chromatograph/Electron Capture Detector/Flame Ionization Detector (GC/ECD/FID).

Calibration checks showed a difference between nominal concentrations and measured concentrations mostly for higher hydrocarbons for the GC/MS data. Based on the observed concentration of the calibration checks, the measured values were corrected after the study period. The corrections were performed by multiplying the measured value by the ratio of the actual calibration mixture concentration versus the observed gas mixture concentration. The GC/MS data, before and after correction, were compared with the canister data from an average 3-hour resolution IOP (Date: 7/24/00, Time: 6 AM) by using scatter plots, box plots, and descriptive statistics.

2. EXPERIMENTAL METHODS

2.1 Instrumentation

2.1.1 Continuous GC/MS

The Entech real-time integrator with an Entech 7100 preconcentrator was used for sample collection and concentration with a Varian 3800 gas chromatograph with FID and column switching valve interfaced to a Varian Saturn 2000 ion trap mass spectrometer for sample analysis.

Under operational conditions, the real-time integrator collected a sample in a 6 L canister by using a vacuum to draw the sample. Samples were integrated over 3-hours non-IOP or 1 hour IOP. At a predetermined time, the preconcentrator would collect a 300 ml subsample from the 6 L canister, focus it and inject it into the GC. The trapping and focusing process consisted of three traps. The first trap (50% glass beads/50% Tenax) trapped sample at -100 °C. The sample was then desorbed from the first trap at 10 °C and transferred to a second trap of 100% Tenax held at -40 °C. The second trap desorbed the sample at 200 °C and transferred it to a third, final focusing trap (a piece of silicosteel capillary) at -180 °C. The sample on the final trap was desorbed at approximately 70 °C to a transfer line heated to 110 °C and connected to the head of the first column. The objective of three-stage trapping process was as follows: 1) the first trap limited the amount of water entering the column by the relatively low desorption temperature, 2) the second trap eliminated CO₂, and 3) the third trap focused the sample so that the injection was made as narrow as possible to limited band broadening. The GC was configured to inject the sample at the head of a 60 m x 0.32 mm polymethylsiloxane column (CPSil-5, Varian, Inc.). This column led into the switching valve set so the effluent went into a 30 m x 0.53 mm GS-GasPro column (J&W Scientific). After approximately 7 minutes, the column switched and the effluent from the first column eluted onto a second 15 m x 0.32 mm polymethylsiloxane column into the mass spectrometer. The column switch was timed to elute the C₂ and C₃ compounds on the FID and all C₄ and higher compounds onto mass spectrometer (Figure 2.1-1).

Diagram of Columns

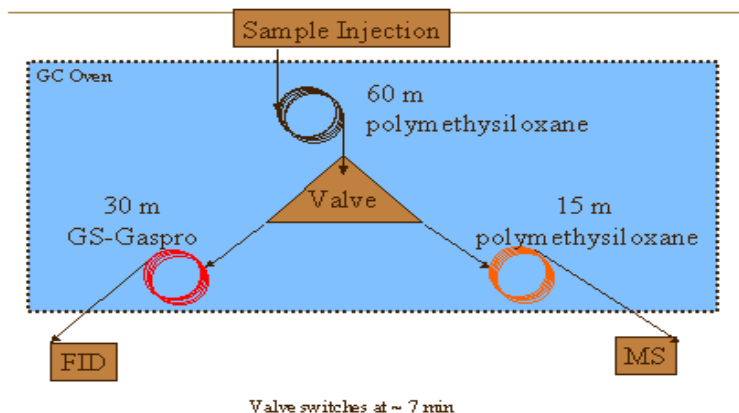


Figure 2.1-1. GC/MS columns.

2.1.2 Canister Samples

Prior to collection, the electropolished canisters were cleaned by alternating evacuation and flushing with humid ultra-high purity air at 140 °C through seven cycles. Ten percent of the cleaned canisters were then pressurized with humid ultra-high purity air, allowed to equilibrate overnight, then analyzed by GC/FID. For a blank value, the total non-methane hydrocarbon concentration was approximately 5 ppbC, well within acceptable values.

Each whole air sample was collected for three hours by pressurized sampling at a flow rate of 40 cc/min to 20-25 psi in stainless steel canisters and analyzed by GC/FID (Figure 2.1-2). A 60 m x 0.32 mm DB-1 capillary column (J & W Scientific, Inc.) was employed to separate the VOCs from C₂-C₁₂ with a temperature program starting at -65 °C for 2 minutes followed by an increase in temperature from 6 °C/minute to 223 °C. A 30 m x 0.53 mm ID PLOT column was used to separate the light VOCs (C₂-C₅) with a temperature program starting at 50 °C for 1 minute followed by an increase in temperature from 12 °C/minute to 200 °C. Helium (Sierra Airgas, UHP) was used as a carrier gas (Goliff and Zielinska, 2001).

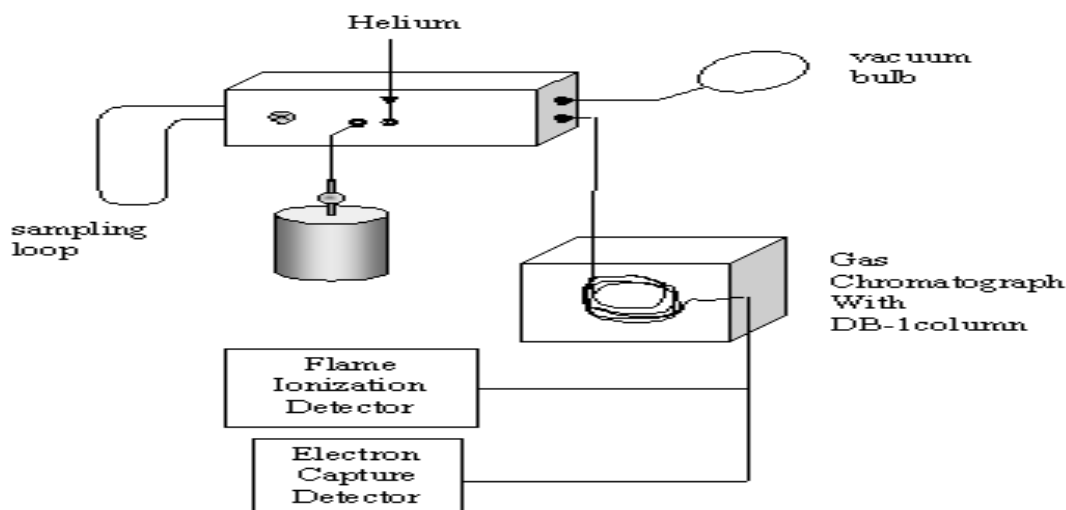


Figure 2.1-2. GC/FID/ECD setup.

2.2 Calibration

2.2.1 Continuous GC/MS

Calibration of the system was conducted with a 112 component mixture that contained the most commonly found hydrocarbons (75 compounds from ethane to n-undecane), halocarbons (23 compounds from F12 to the dichlorobenzene), and oxygenated compounds (14 compounds from acetaldehyde to nonanal, including MTBE). The standards were prepared in 6 L silco-steel canisters (Restek, Bellefonte, PA) by mixing three different standards through a multi-valve manifold using a Baratron absolute capacitance manometer (MKS Instruments, Andover, MA) to determine the pressure each standard added to the mixture. Prior to mixing, approximately 0.2 ml of ultrapure water was added to the canister to humidify the mixture—in prior experiments without the added humidity the oxygenated compounds were much lower in response. A 74 component hydrocarbon mix was purchased from Air Environmental, Inc. with compounds from 0.2 to 10 ppbv. A 14 component oxygenated compound standard (1.0 ppbv) with one hydrocarbon for reference was also purchased from Air Environmental, Inc. The 23 component halocarbon mixture was purchased from Scott Specialty Gases with concentrations between 5 and 10 ppbv. The minimum detection limits (MDL) for volatile hydrocarbons and halocarbons were 0.1 ppbv and 0.01 ppbv for carbonyl compounds.

After the instruments were operational, a three-point calibration was conducted and a sampling sequence for ambient samples was started (every three hours starting at midnight). One calibration check and one blank of zero air were analyzed daily (at 0400 and 0500 hr).

During the study, IOPs were defined by air quality forecasting when high levels of ozone were expected. During IOPs, ambient samples were collected every hour and three-point calibrations were generally run prior to each IOP. Personnel were generally on-site during all IOPs, partly because of the need to run other instrumentation, and were generally not on-site during non-IOPs. When personnel were not present, remote access software was used to check instrument status and confirm that it was operating normally. Occasionally the instruments were taken off-line to bake out the ion trap or perform other maintenance, i.e., data capture was not 100% (Sagebiel and Zielinska, 2001). Two ion traps had to be disassembled and cleaned during the study and columns needed replacement, but generally the instruments performed well. Instrument tuning was also very important for consistent data since the instruments were not stable over the entire study period. Autotuning is timely, however, and was difficult to perform on a regular basis.

2.2.2 Canisters

The GC/FID response is calibrated in ppbC using primary calibration standards traceable to the National Institute of Standards and Technology (NIST) Standard Reference Materials (SRM). The NIST SRM 1805 (254 ppb of benzene in nitrogen) was used for calibrating the analytical system for C₂-C₁₂ hydrocarbon analysis. The 1.0 ppm propane in nitrogen standard (Scott Specialty Gases, periodically traced to SRM 1805) was used to calibrate the light hydrocarbon system. Based on the uniform carbon response of the FID to hydrocarbons, the response factors determined from these calibration standards were used to convert area counts into concentration units (ppbC) for every peak in the chromatogram.

Identification of individual compounds in air samples were based on the comparison of linear retention indices (RI) with RI values of authentic standard compounds and RI values obtained by other laboratories performing the same type of analysis using the same chromatographic conditions (Auto/Oil Program, Atmospheric Research and Exposure Assessment Laboratory, EPA). The Desert Research Institute (DRI) laboratory calibration table contains 160 species. Three to five concentration levels of the standard, with two to three injections per calibration level, were used to generate calibration curves (U.S. EPA).

2.3 Description of Research Sites

Research sites (Figure 2.3-1) were intended to provide high quality time-resolved chemical and other aerometric data. Research sites were: 1) Downwind of Sacramento (Granite Bay), 2) Fresno (Parlier), and 3) between Oakland and Livermore (Sunol).

Granite Bay: situated downwind from Sacramento in Placer County. Suburban area with limited local traffic

Parlier: situated at Kerney Experimental Agricultural Station (University of California, Davis) in Fresno County surrounded by vegetation and downwind from Fresno metropolitan area.

Sunol: located at the top of the Sunol Hill (140 m elevation) between interstate I-680 and Highway 84 in Alameda County (busy during morning and afternoon commuting traffic), downwind from the Bay Area.

Granite Bay

Longitude: -121.17

Latitude: 38.75

Height: 227 meter

On school property away from traffic with occasional school bus traffic.

Sunol

Longitude: -121.5940

Latitude: 37.5940

Height: 140 meter

Mixed site with many trees located in a power system communication building with backup propane generator power. Vehicle exhaust had most effect on site.

Parlier

Longitude: -119.714

Latitude: 36.825

Height: 166 meter

Near an agricultural site with farming equipment exhaust which caused peaks for certain compounds.

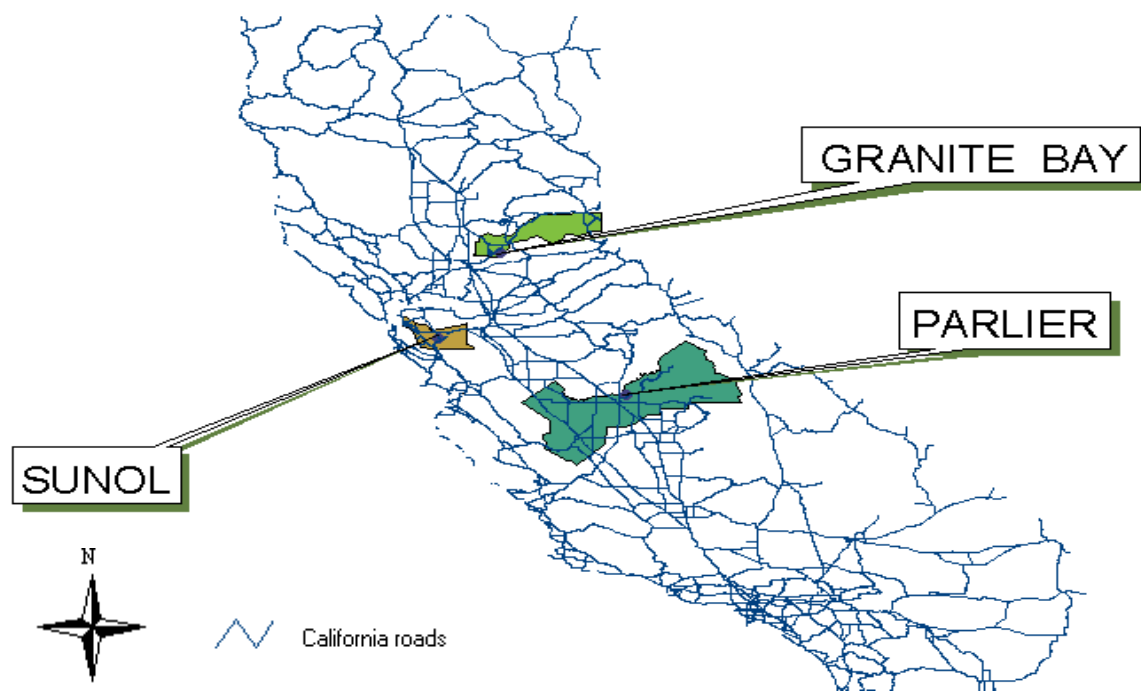


Figure 2.3-1. The location of three research sites.

3. RESULTS AND DISCUSSION

3.1 Calibration and Calibration Checks

The multipoint calibration (three concentrations + zero point) was performed before each IOP episode at 4 AM and for non-IOP episodes at 1 AM using a freshly prepared pressurized canister from DRI (Reno) at the following concentrations: 1 AM (100 mL), 4 AM (200 mL), and 7 AM (400 mL)

When performing calibration checks (daily at 4 AM), the difference between nominal concentrations and measured concentrations were observed mostly for higher hydrocarbons. The difference was probably caused by lower canister pressure over time that resulted in the “sticking” of the heavier hydrocarbons to the walls of the canister. Based on the observed concentration of the calibration checks, the measured values were corrected after the study period.

3.2 Data Correction

3.2.1 Granite Bay

Comparison between canister data and GC/MS data is very important to check for calibration bias. The comparison of canister data and GC/MS data for the three sites was conducted on the 54 PAMS compounds by using mixing ratio plots, scatter plots, box plots, and descriptive statistics. Corrections for GC/MS data were performed by multiplying the measured value by the ratio of the actual calibration mixture concentration versus observed gas mixture concentration.

Figure 3.2-1 shows the ratio of actual calibration mixture concentration versus observed gas mixture concentration for various VOCs (target ratio = 1). The ratio decreases for heavy hydrocarbons and increases for light hydrocarbons. When the ratio decreases, the observed gas mixture concentration is higher than the actual calibration mixture concentration.

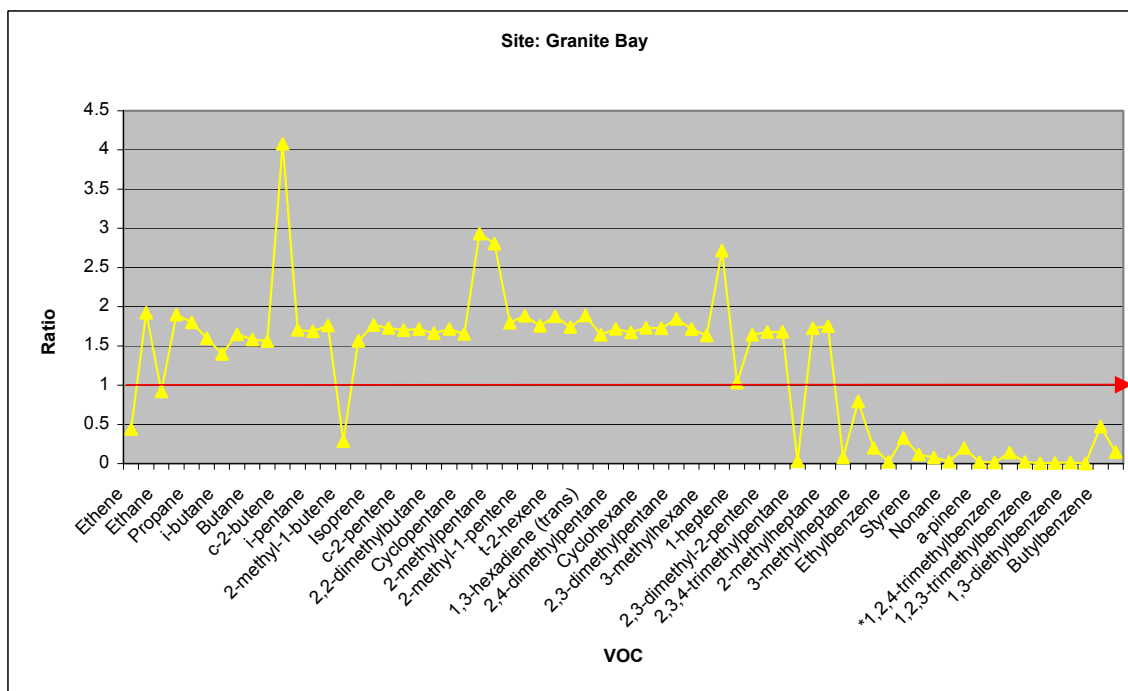


Figure 3.2-1. Ratio of actual calibration mixture concentration versus observed gas mixture concentration for various VOCs.

3.2.2 Sunol

For Sunol, the light hydrocarbons were overestimated especially for isoprene. The difference in isoprene concentrations was due to incorrect SATURN programming—the sequence cut was on the isoprene peak itself causing incorrect calibration. Alkenes gave higher values for GC/MS data than for canister data. The double bonded compounds were probably more effected by the change in pressure of the calibration mixture. The C₅ hydrocarbon had problems with tailing peaks caused by either a high or low injection temperature, or low oven temperature. The Module 3 Entech heater had problems due to lack of nitrogen gas, according to the log book, and was corrected.

A propane generator was located on the roof near the GC/MS that may have been a source of light hydrocarbons possibly effecting the measurements. The inlet to the canister sampler, however, was at ground level resulting in no added affect to the samples. The generator at Sunol ran once a week every Tuesday (except 9/12/00 and 9/19/00) for about 20 minutes from 10:00 to 10:30 PST. The propane concentration was not significantly higher for measurements taken on 7/25/00 and 8/1/00, days when the generator was scheduled to run.

The incorrect sequence cut for the isoprene peak caused the incorrect quantification of isoprene concentrations. After calculating the linear formula for isoprene, the data was corrected. The linear formula for the Saturn method was $y=1.2760X$, and the linear formula of the calibration was $y=167.69X$. The data was corrected by multiplying the measure value

by the ratio of the actual gas mixture concentration versus observed gas mixture concentration. Figure 3.2-2 shows the ratio for various hydrocarbons.

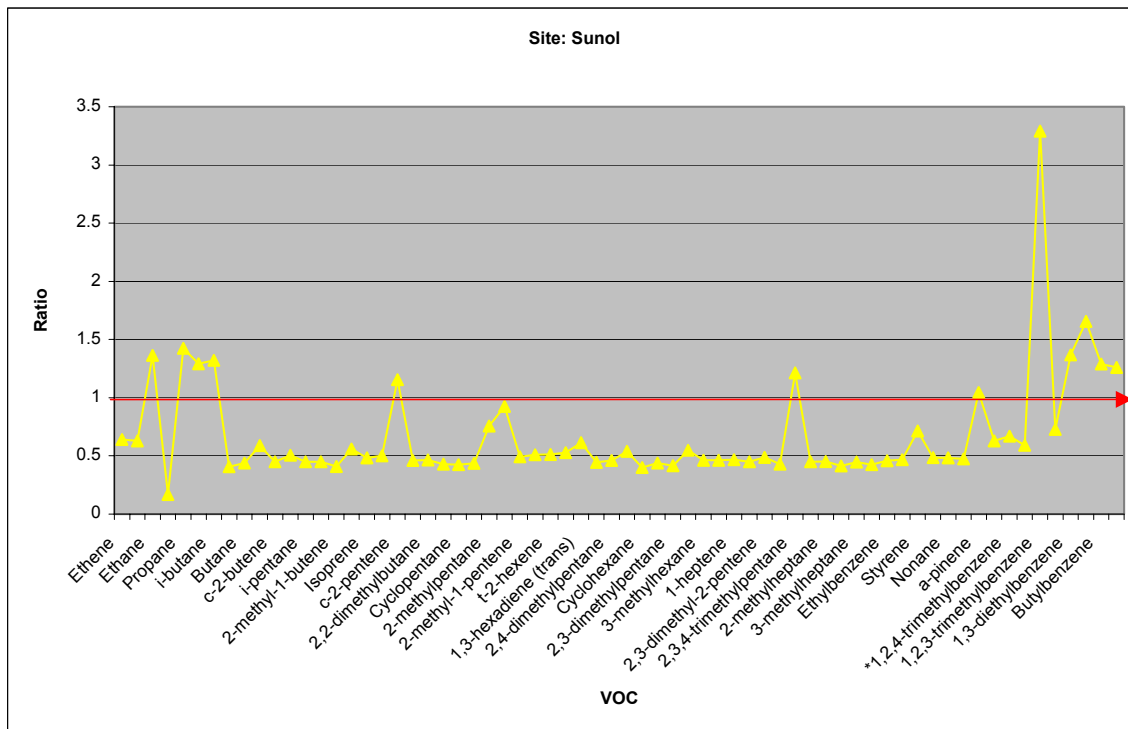


Figure 3.2-2: Ratio of actual calibration mixture concentration versus observed gas mixture concentration for various VOCs.

3.2.3 Parlier

The Parlier data had inconsistent light hydrocarbon and heavy hydrocarbon data. The inconsistencies were possibly caused by improper heating of the Entech Module 3 due to insufficient liquid nitrogen tank pressure. According to the logbook, the GC/MS ran out of liquid nitrogen on 9/17/00 and 9/18/00. The Parlier data also has high background ions in the spectra possibly due to column bleed that effected the calibration and caused misidentification of the peaks. Parlier also had problems with the air conditioner resulting in high freon values. The correction of the data was done by multiplying the measured value by the ratio of the actual gas mixture concentration versus the observed gas mixture concentration.

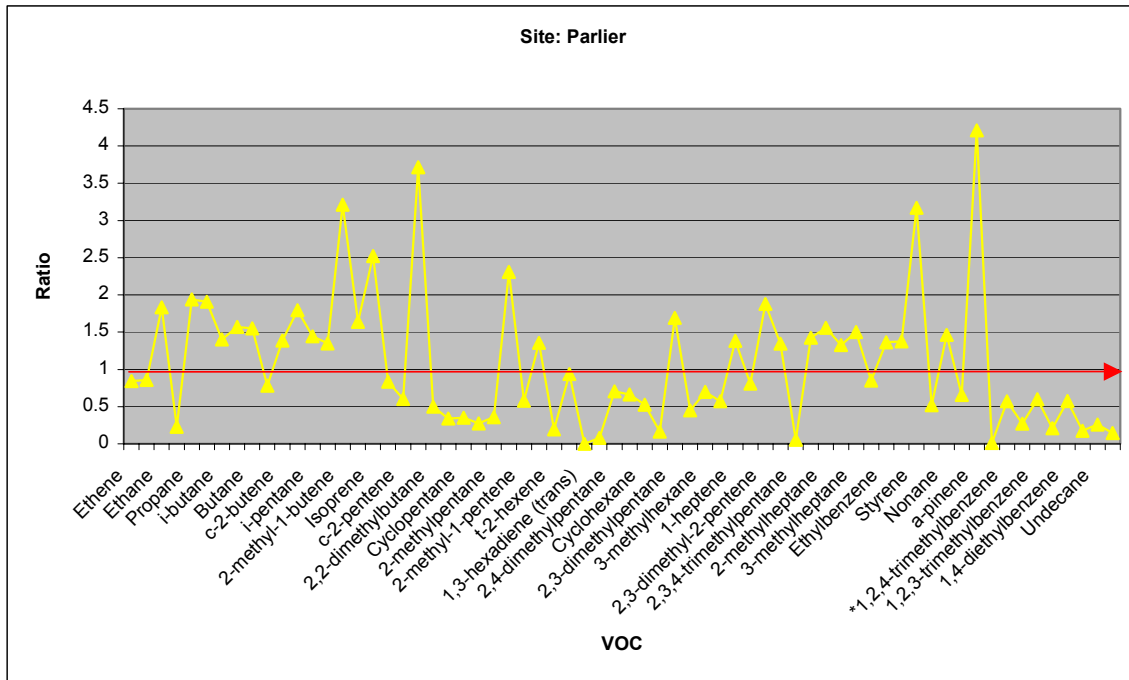


Figure 3.2-3. Ratio of actual calibration mixture concentration versus observed gas mixture concentration for various VOCs.

Figure 3.2-3 shows the observed gas mixture concentration has lower concentration than the actual calibration mixture concentration for most light hydrocarbons and higher concentrations for heavy hydrocarbons.

3.3 Data Episode 1 (Date: 7/24/00, Time: 6 AM)

3.3.1 Granite Bay

Figures 3.3-1 and 3.3-2 compare the mixing ratios (ppbC) of the 54 PAMS compounds before and after correction, respectively.

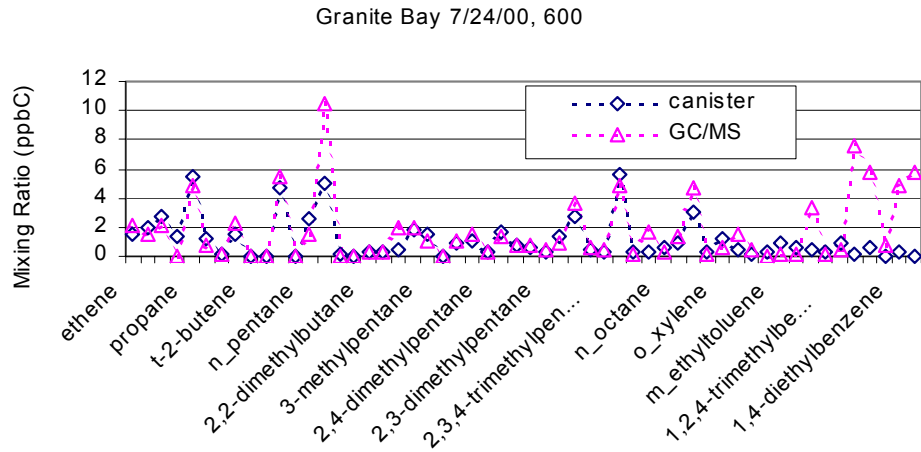


Figure 3.3-1: The comparison of the 54 PAMS species before correction.

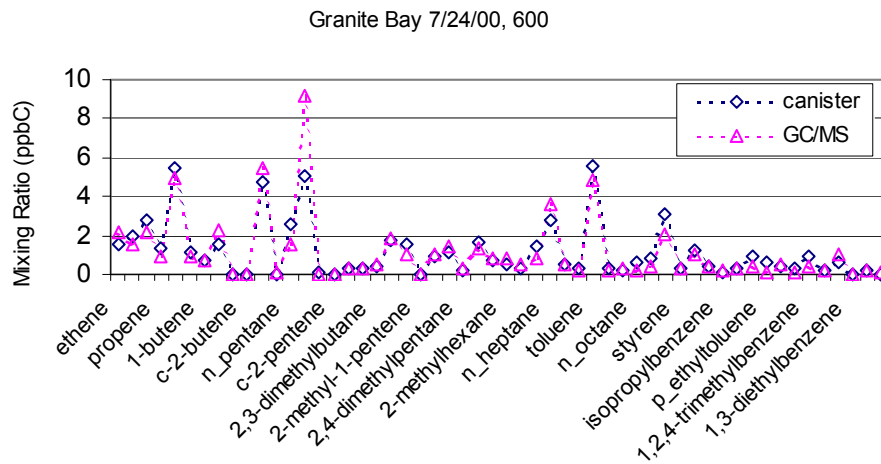


Figure 3.3-2: The comparison of the 54 PAMS species after correction.

Figure 3.3-2 shows the GC/MS heavy hydrocarbons are better correlated to the canister heavy hydrocarbons after correction.

Figures 3.3-3 and 3.3-4 show scatter plots of 54 PAMS compounds before correction and after correction, respectively.

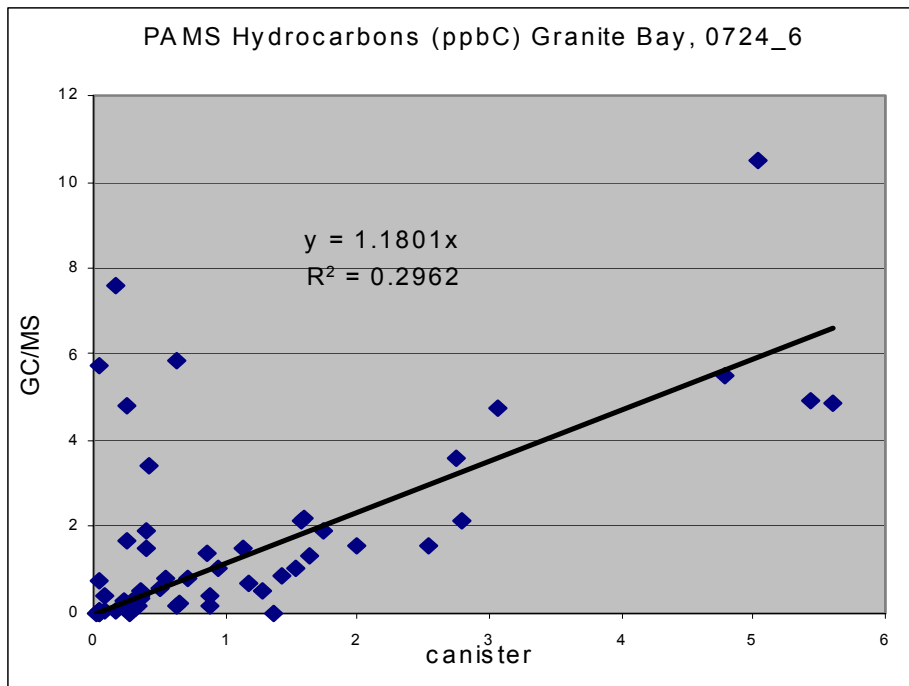


Figure 3.3-3: Scatter plot comparing canister data versus GC/MS data before correction.

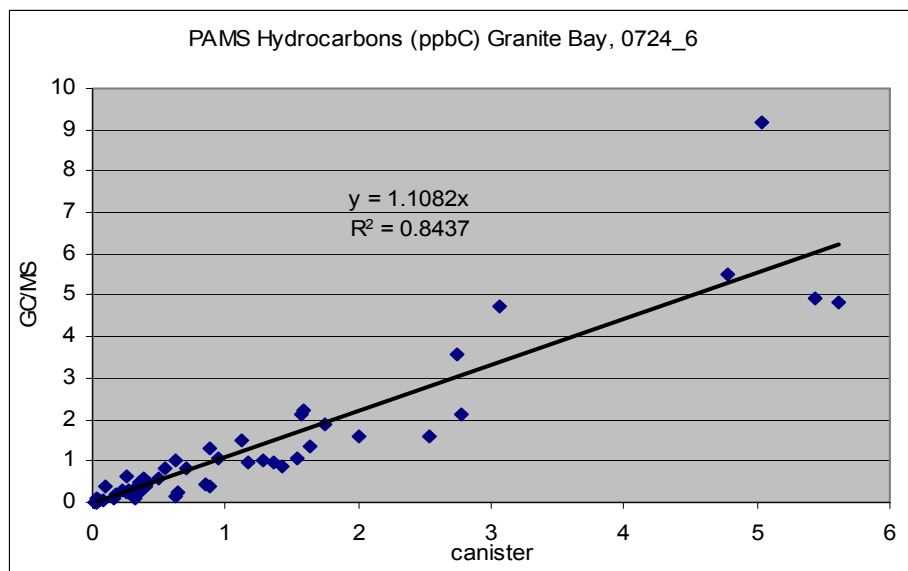


Figure 3.3-4: Scatter plot comparing canister data versus GC/MS data after correction.

Figure 3.3-3 shows the correlation between the GC/MS data and the canister data is poor ($R^2 = 0.296$). The corrected data in Figure 3.3-4 is much improved ($R^2 = 0.844$).

Below are two box plots that compare the GC/MS data and canister data before correction (Figure 3.3-5) and after correction (Figure 3.3-6).

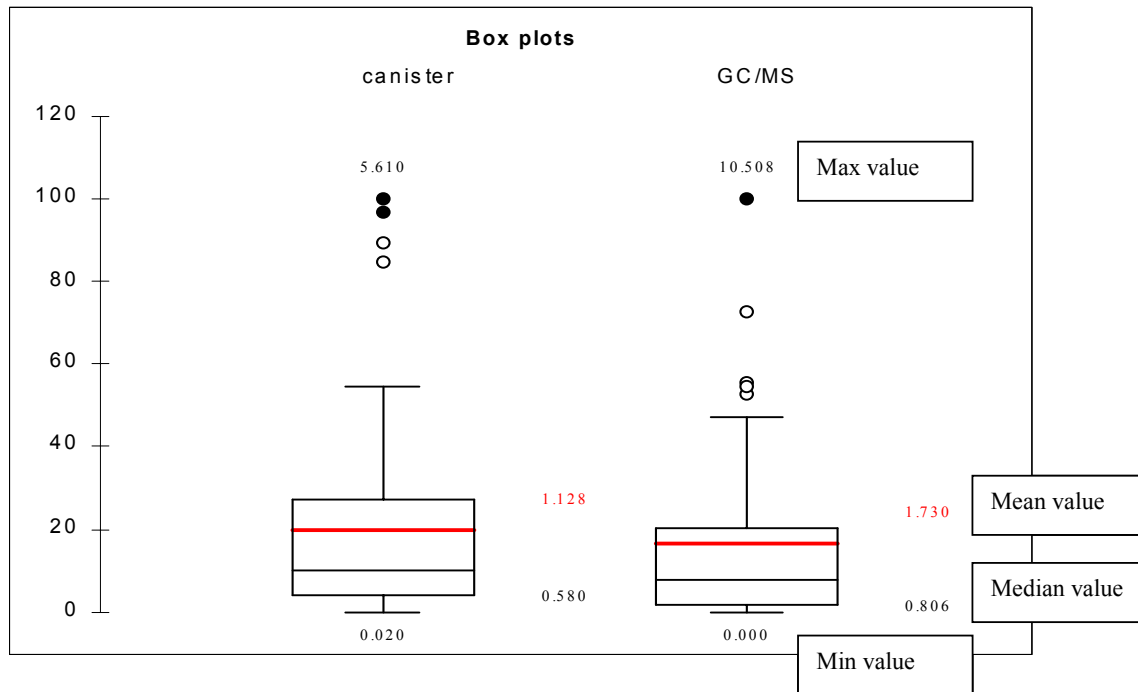


Figure 3.3-5: Box plots for GC/MS data and canister data before the correction.

Figure 3.3-5 shows the mean and the median is different for canister and GC/MS data. The distance between the median and upper fence is an indication of right skewness, which is similar for the GC/MS data and the canister data. The interquartile range (3rdquartile-2ndquartile) is an indication of where the middle half of the data lies (1.918 for the GC/MS data and 1.29 for the canister data).

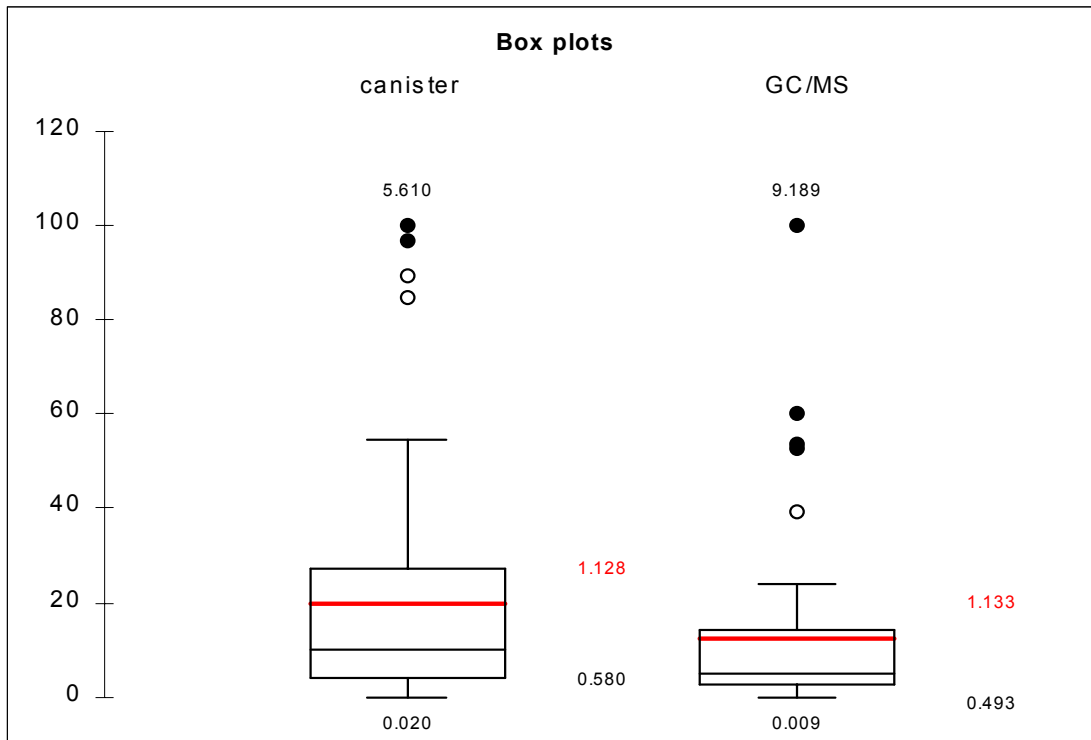


Figure 3.3-6: Box plots comparing canister data and GC/MS data after correction.

After correction of the data (Figure 3.3-6), the canister and GC/MS data have similar mean values, 1.128 and 1.133 respectively. The interquartile range (3rdquartile-2ndquartile) after correction is 1.084 for the GC/MS data, more comparable to the canister data of 1.29. The variance of the GC/MS data after correction was lowered resulting in an improved data set.

3.3.2 Sunol

Below are two figures that compare the mixing ratio (ppbC) of the 54 PAMS species before correction (Figure 3.3-7) and after correction (Figure 3.3-8).

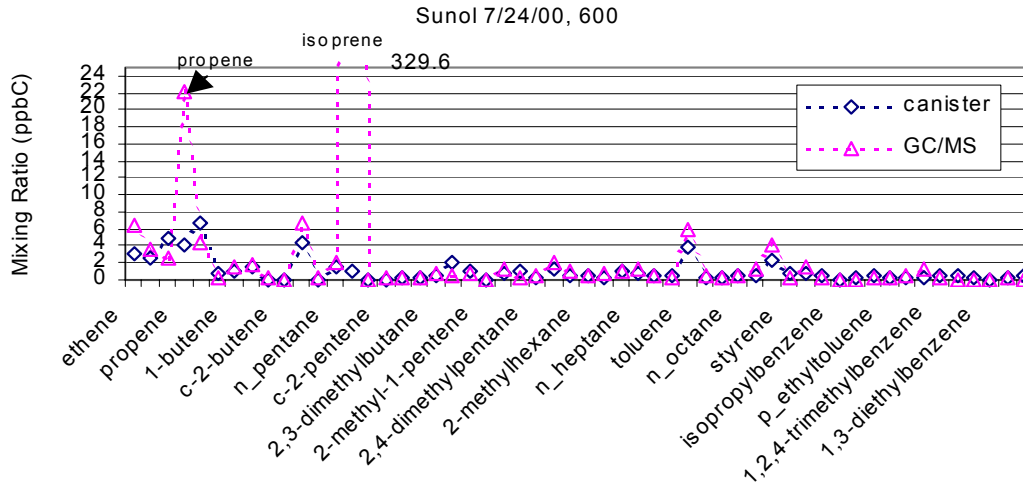


Figure 3.3-7: The comparison between canister data and GC/MS data for the 54 PAMS compounds.

Figure 3.3-7 shows a large difference between the isoprene and C₅ hydrocarbons concentrations of the GC/MS and canister data.

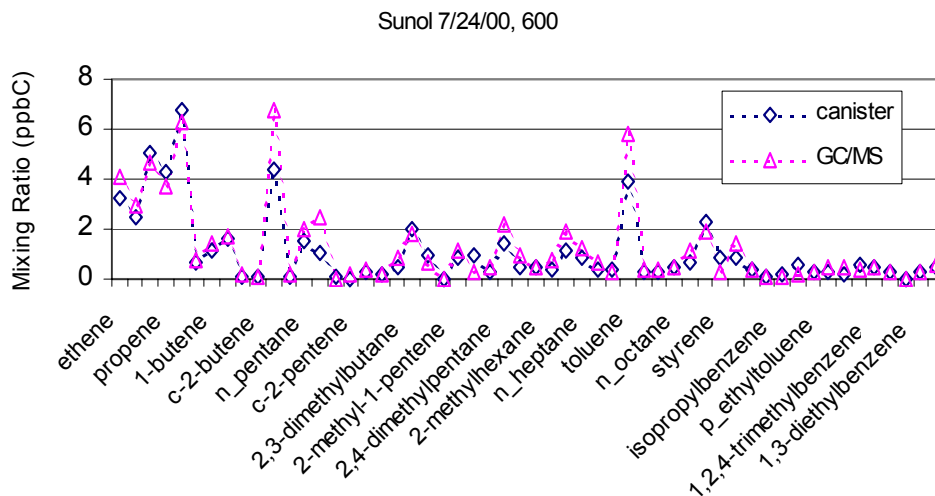


Figure 3.3-8: The comparison between canister data and GC/MS data for the 54 PAMS compounds after correction.

Figure 3.3-8 shows the concentrations of the 54 PAMS compounds of the corrected GC/MS data compared to the canister data. The GC/MS and canister data are more comparable, especially isoprene.

Figures 3.3-9 and 3.3-10 show scatter plots comparing the GC/MS data and canister data before and after correction, respectively.

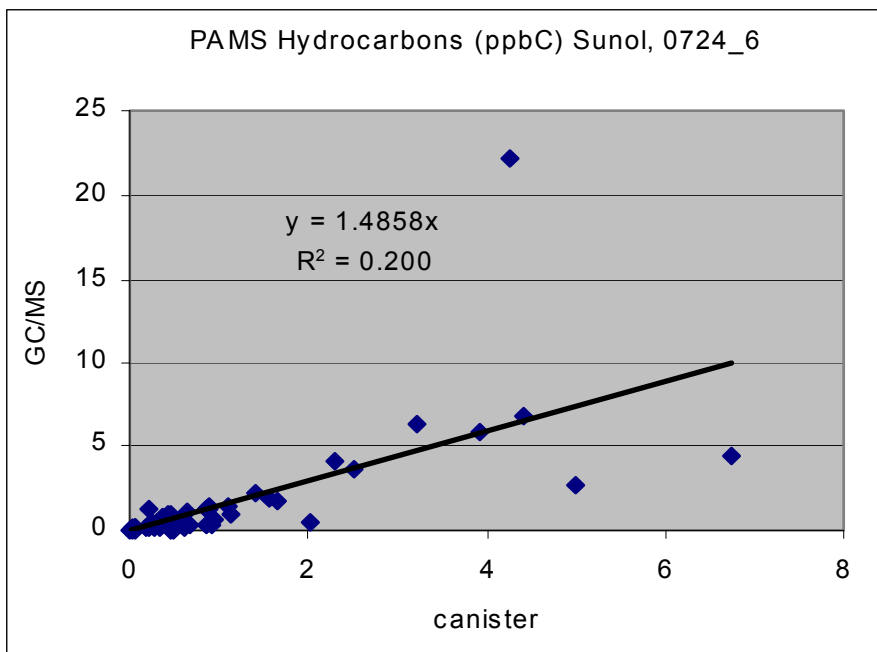


Figure 3.3-9: Scatter plot between GC/MS data and canister data before correction.

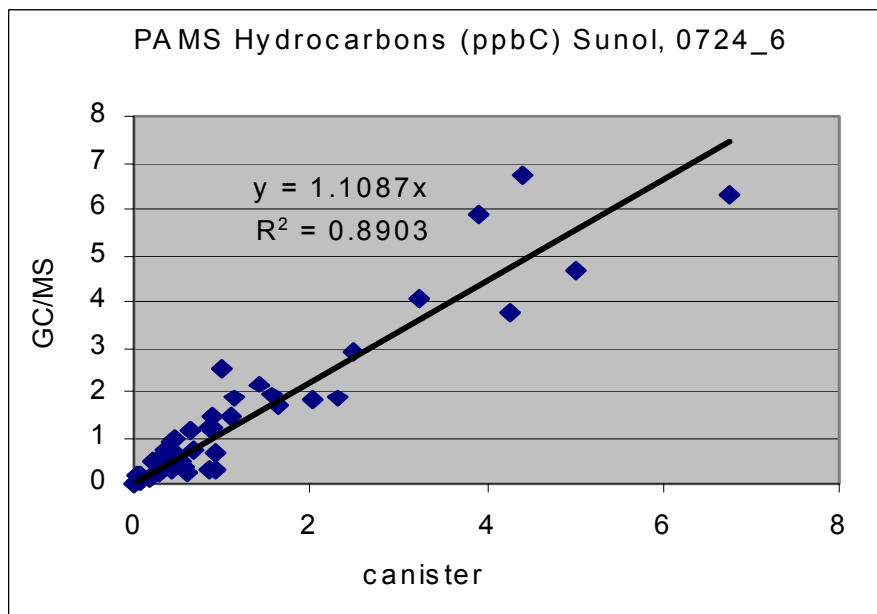


Figure 3.3-10: Scatter plot after correction between the canister data and the GC/MS data.

Figure 3.3-9 shows a correlation between the GC/MS data and the canister data ($R^2 = 0.4341$). Figure 3.3-10 shows the correlation between GC/MS data and the canister data has improved after correction ($R^2 = 0.8903$).

Figures 3.3-11 and 3.3-12 show box plots comparing canister data and GC/MS data before correction and after correction, respectively.

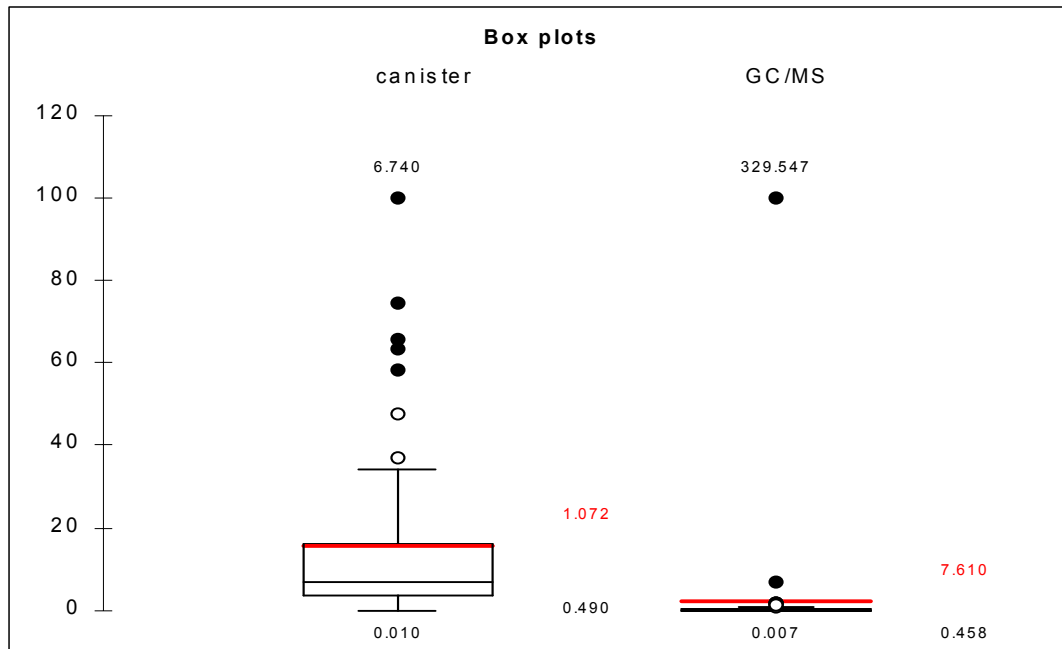


Figure 3.3-11: Box plots before correction between the canister data and the GC/MS data.

Figure 3.3-11 shows a large difference between the mean of the canister data and the GC/MS data: mean of canister is 1.072, and mean of GC/MS data is 7.610. The interquartile range is 1.251 for the GC/MS data and 0.84 for the canister data.

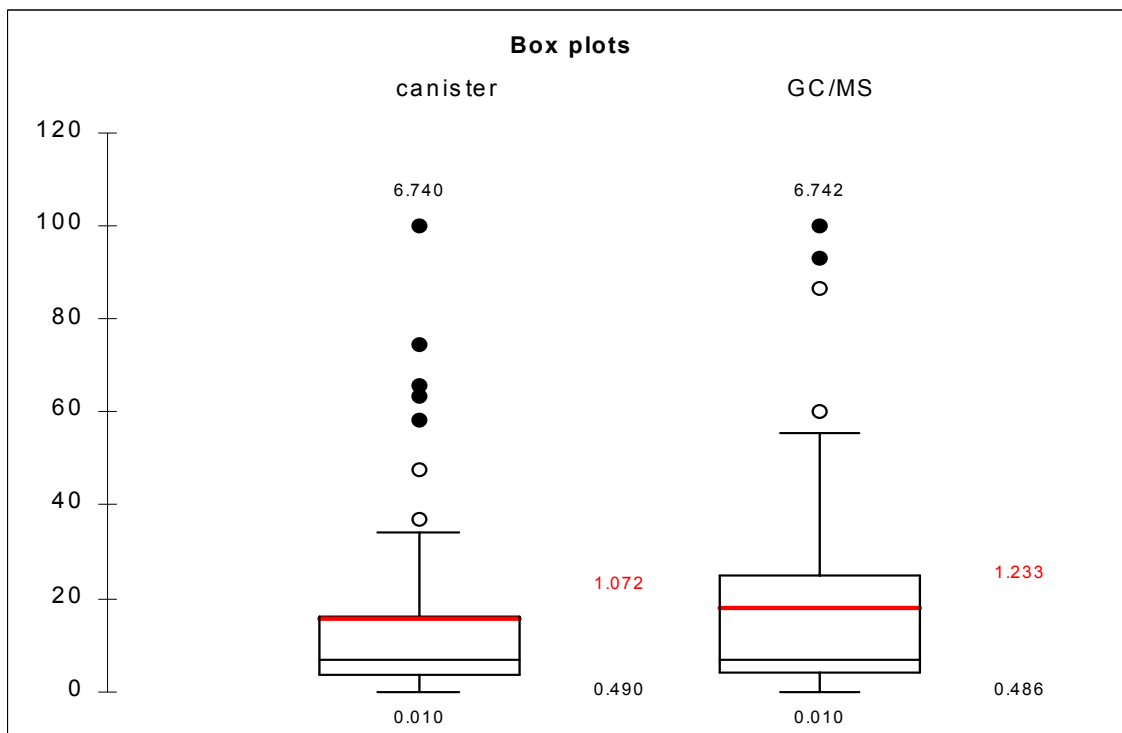


Figure 3.3-12: The same box plots after correction for the canister data and the GC/MS data.

After correction, Figure 3.3-12 shows the mean of the two data sets are similar: 1.233 for the GC/MS data compared to 7.610 before data correction. The interquartile range also increased for the GC/MS data to 1.4213 making the difference between the interquartile range for the canister and GC/MS data greater.

3.3.3 Parlier

The two figures below (Figures 3.3-13 and 3.3-14) show the response of the 54 PAMS compounds before and after correction, respectively.

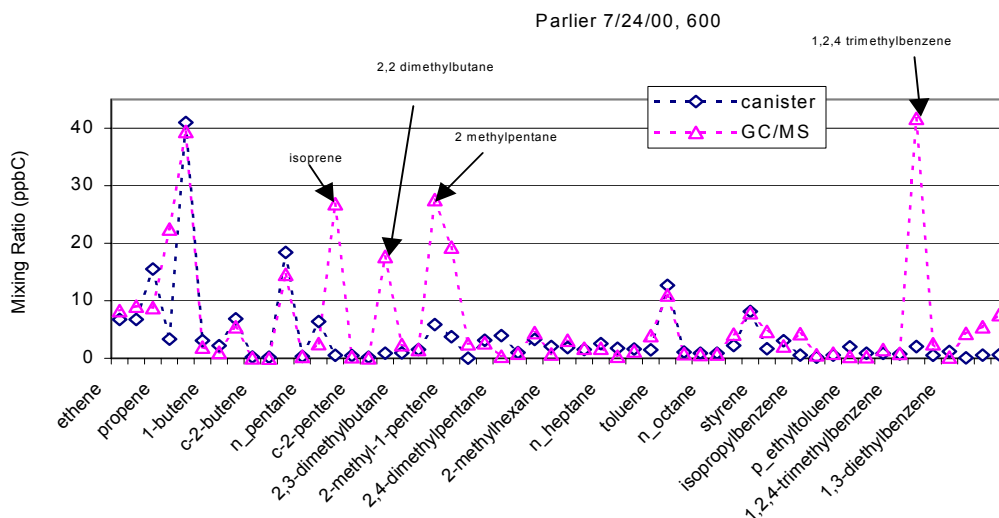


Figure 3.3-13: The comparison before correction between canister data and GC/MS data for the 54 PAMS compounds.

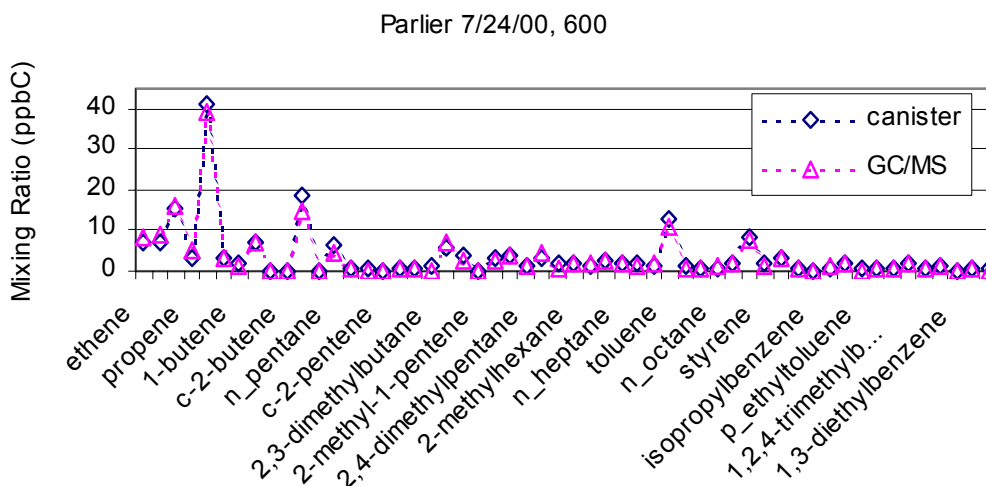


Figure 3.3-14: The comparison after correction between canister data and GC/MS data for the 54 PAMS compounds.

Figure 3.3-13 shows the canister and GC/MS data before correction. There is a large difference in light hydrocarbon (namely isoprene, 2,3-dimethylbutane, and 2-methylpentane concentrations) and heavy hydrocarbon concentration between the canister and GC/MS data. Figure 3.3-14 shows after correction the difference between the canister and GC/MS data is markedly improved.

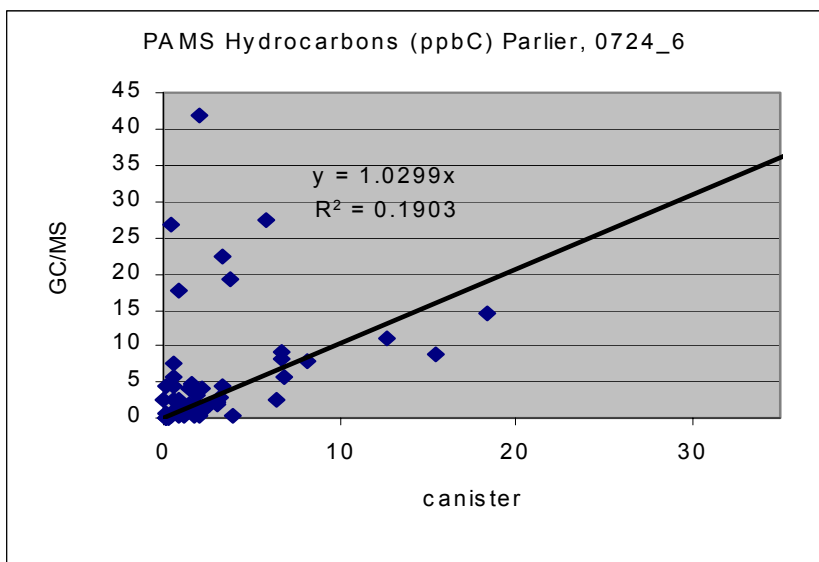


Figure 3.3-15: Scatter plot between the canister data and the GC/MS data before correction.

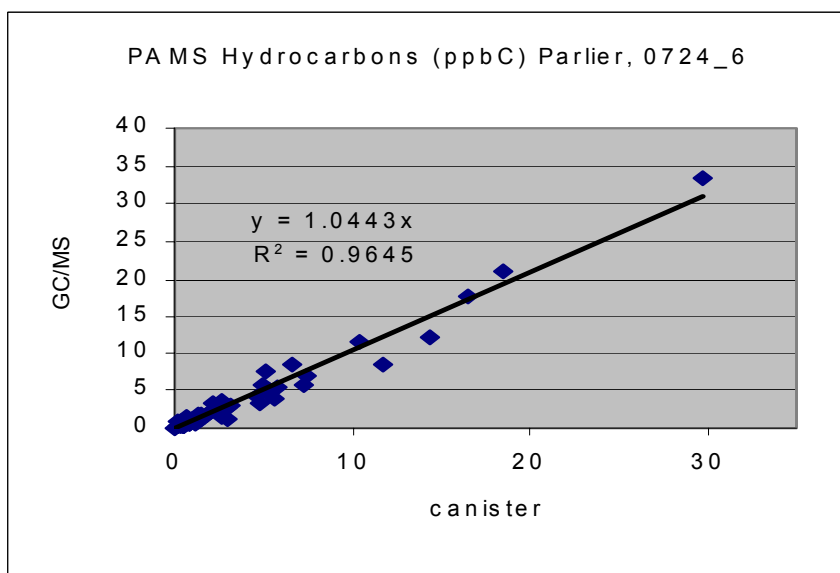


Figure 3.3-16: Scatter plot between the canister data and the GC/MS data after correction.

Before correction, Figure 3.3-15 shows a poor correlation between the GC/MS data and the canister data ($R^2 = 0.190$). After correction, Figure 3.3-16 shows a good correlation between the GC/MS and canister data ($R^2 = 0.964$).

Below are two box plots that compare the GC/MS data and canister data before correction (Figure 3.3-17) and after correction (Figure 3.3-18).

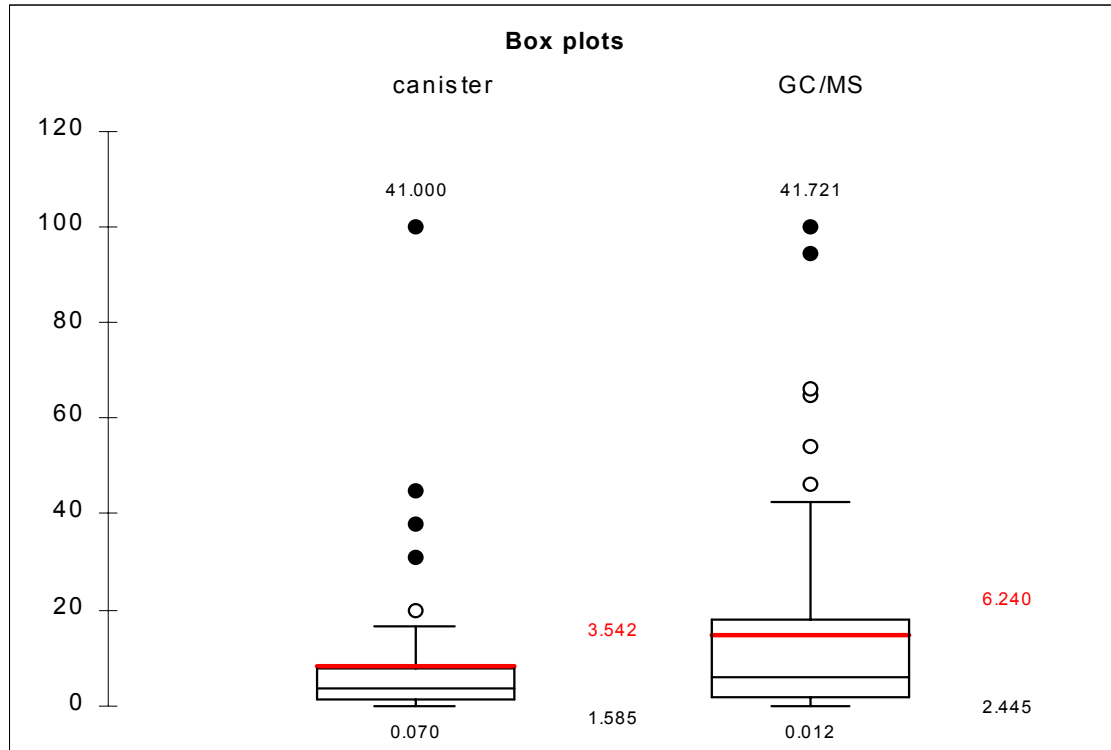


Figure 3.3-17: Box plots before correction between the canister and GC/MS data.

Figure 3.3-17 shows a large difference between the mean of the canister data and the GC/MS data: the mean equals 3.542 for the canister data and 6.240 for the GC/MS data. The interquartile range is also different between the GC/MS and the canister data, notably 6.828 for the GC/MS data and 2.710 for the canister data. The right skewness is less pronounced in the canister data than the GC/MS data.

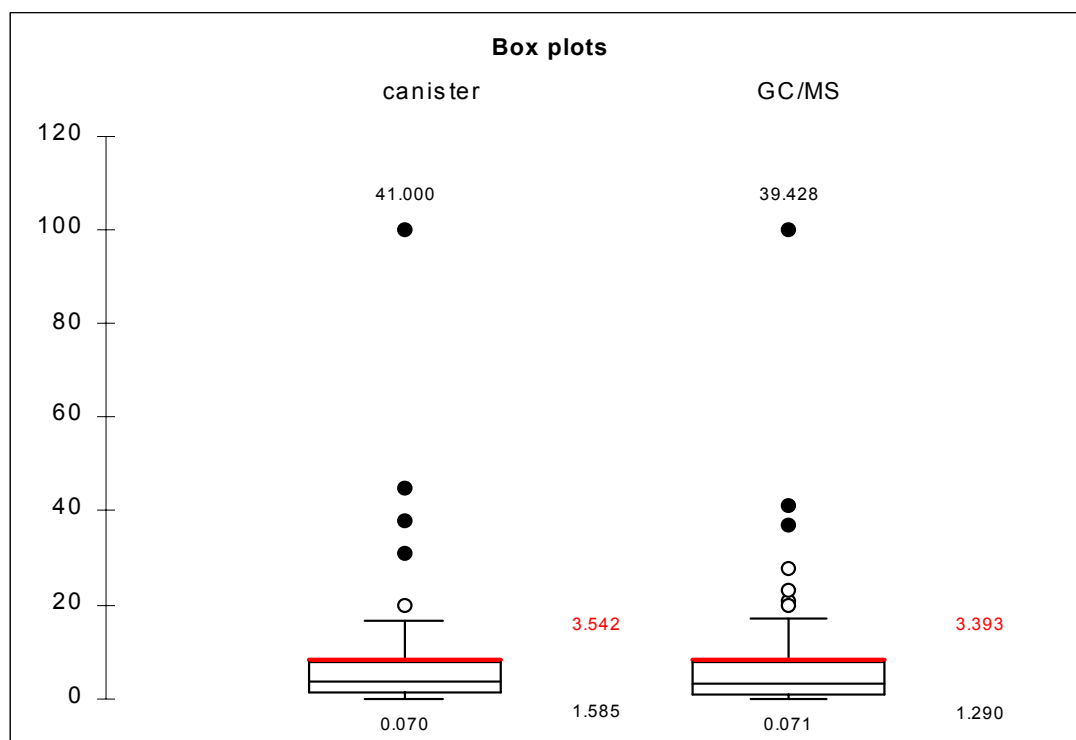


Figure 3.3-18: Box plots after correction between the canister data and the GC/MS data.

Figure 3.3-18 shows the mean and median values are very similar for the GC/MS and canister data after correction. The interquartile range is also more similar for the GC/MS and the canister data (2.792 for the GC/MS data and 2.710 for the canister data), and the right skewness and distribution are similar.

4. CONCLUSION

The correction process improved the GC/MS data for all three sites.

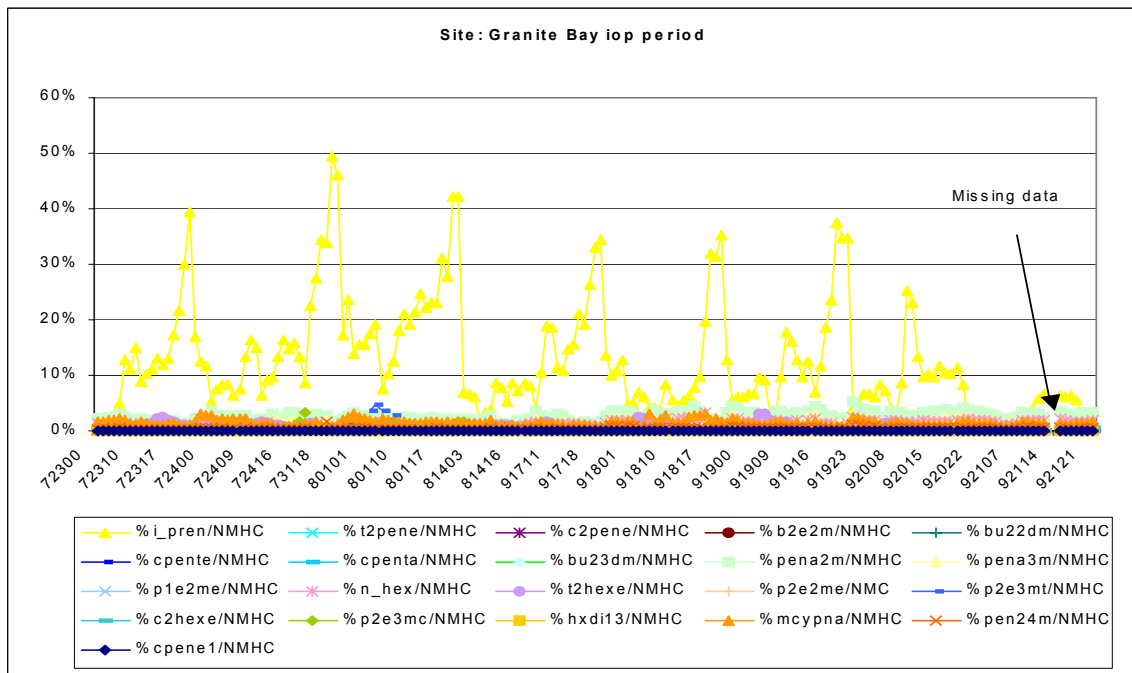
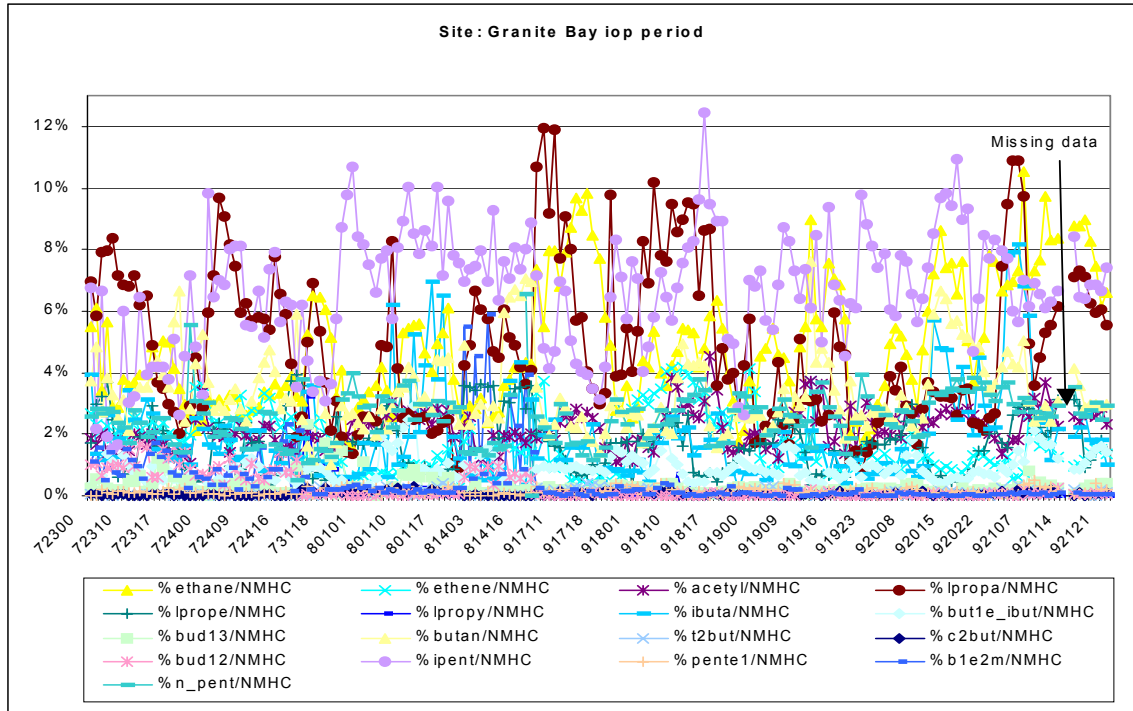
- 1) The GC/MS data was corrected by multiplying the measured value by the ratio of the actual calibration mixture concentration versus the observed gas mixture concentration.
- 2) Scatter plots for the three sites showed the correlation between the canister and GC/MS data improved after the correction process.
- 3) Box plots for all three sites showed that the distribution between the canister data and the GC/MS data improved after correction.

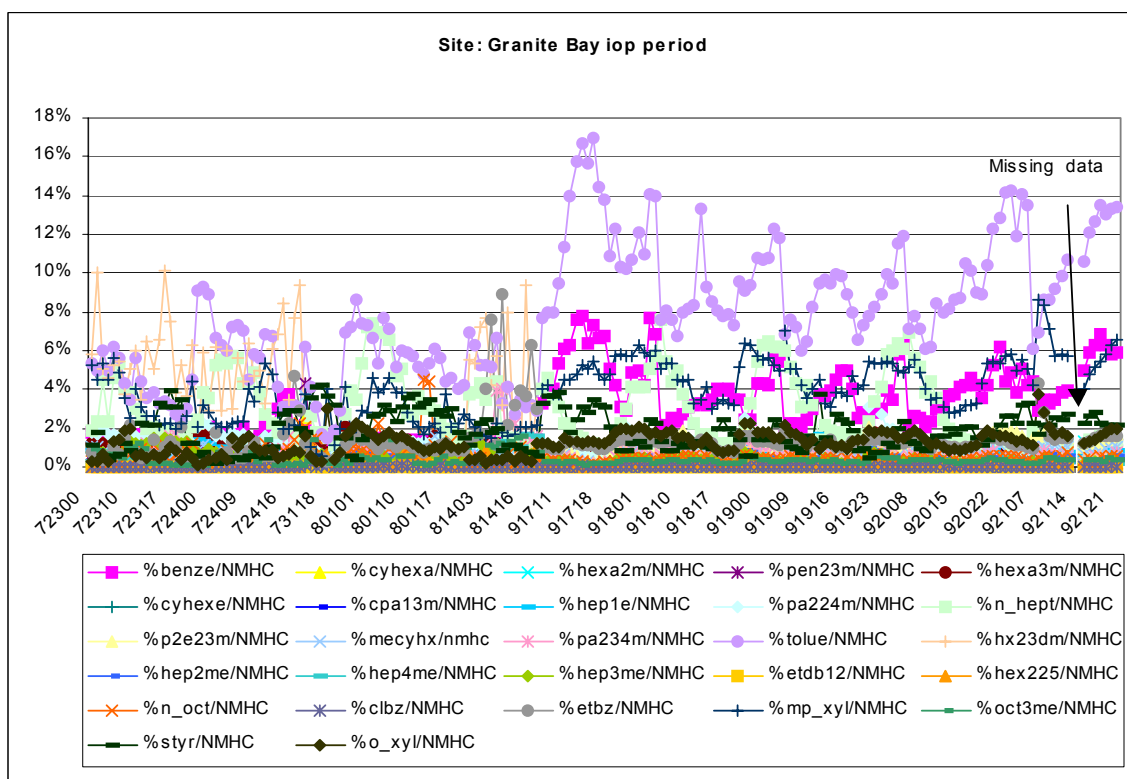
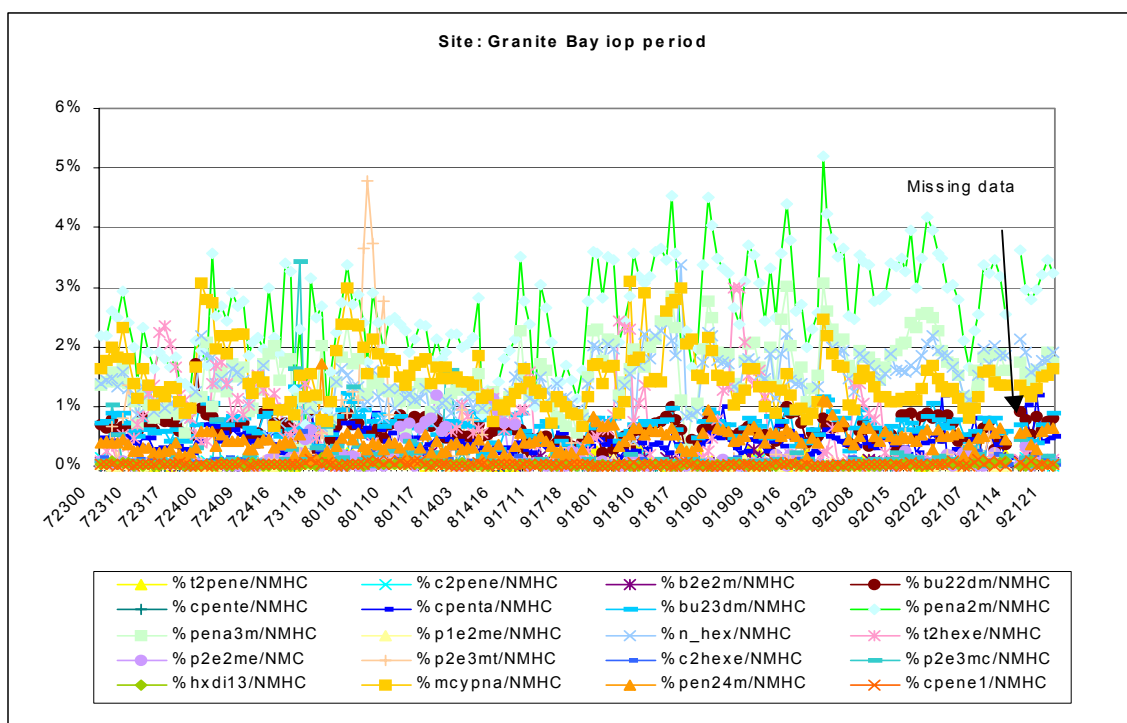
5. REFERENCES

- Goliff, W.S. and B. Zielinska (2001). Hydrocarbons Measurements During the Central California Ozone Study. Paper 694, presented at Air & Waste Management Association 94th National Meeting.
- Fujita, E.M., R. Keislar, W. Stockwell, D. Freeman, J. Bowen, R. Tropp, S. Tanrikulu and A. Ranzieri (2000). Central California Ozone Study – Volume II Field Operations Plan. California Air Resources Board.
- Sagebiel, J.C. and B. Zielinska (2001). Setup and Operation of an Automated GC/MS for Ambient Air Sample Collection and Analysis. Paper 386, presented at Air & Waste Management Association 94th National Meeting.
- U.S. EPA, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, “Compendium Method TO-15: Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatograph/Mass Spectrometry (GC/MS),” EPA/625/R-96/010b.

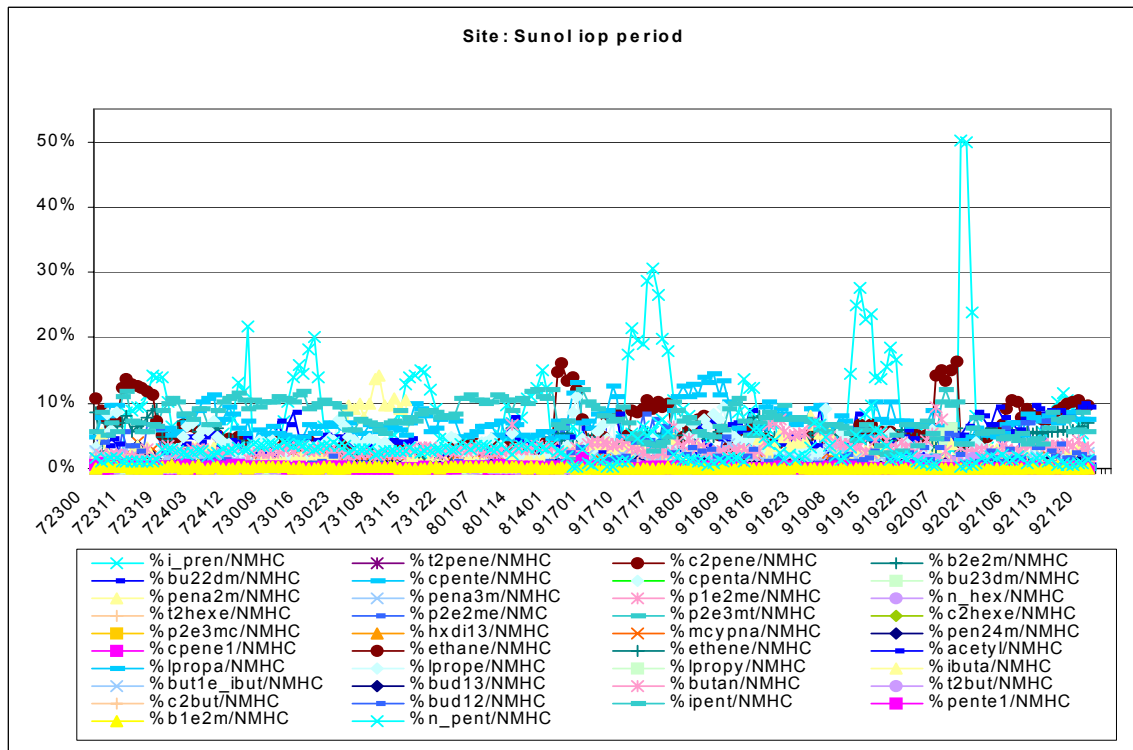
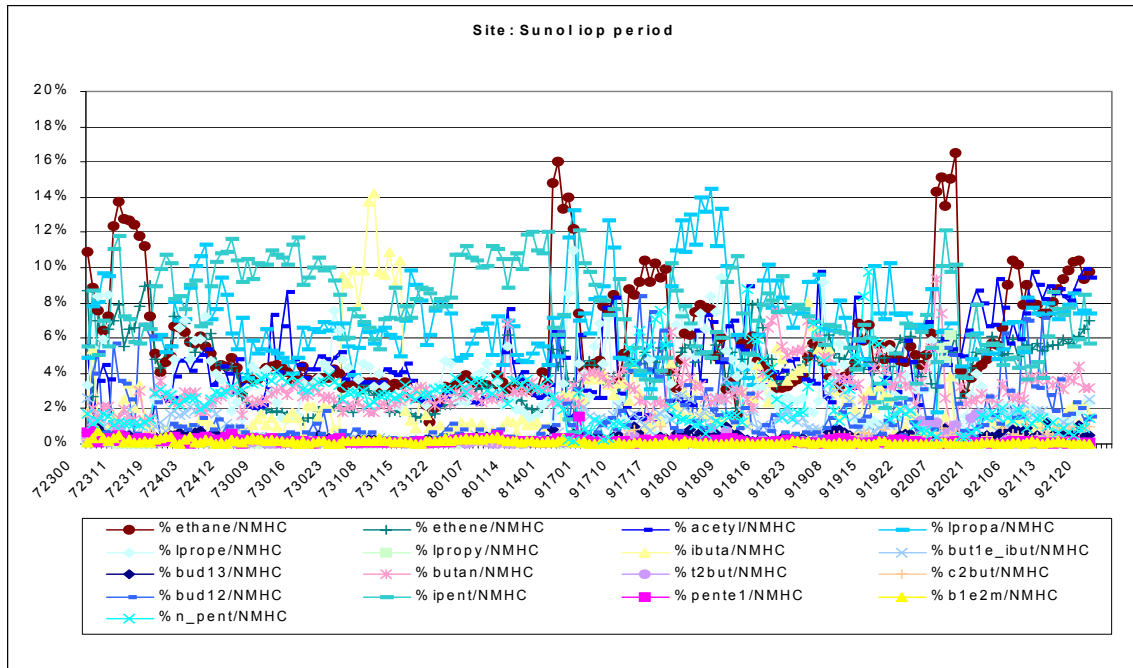
6. APPENDICES

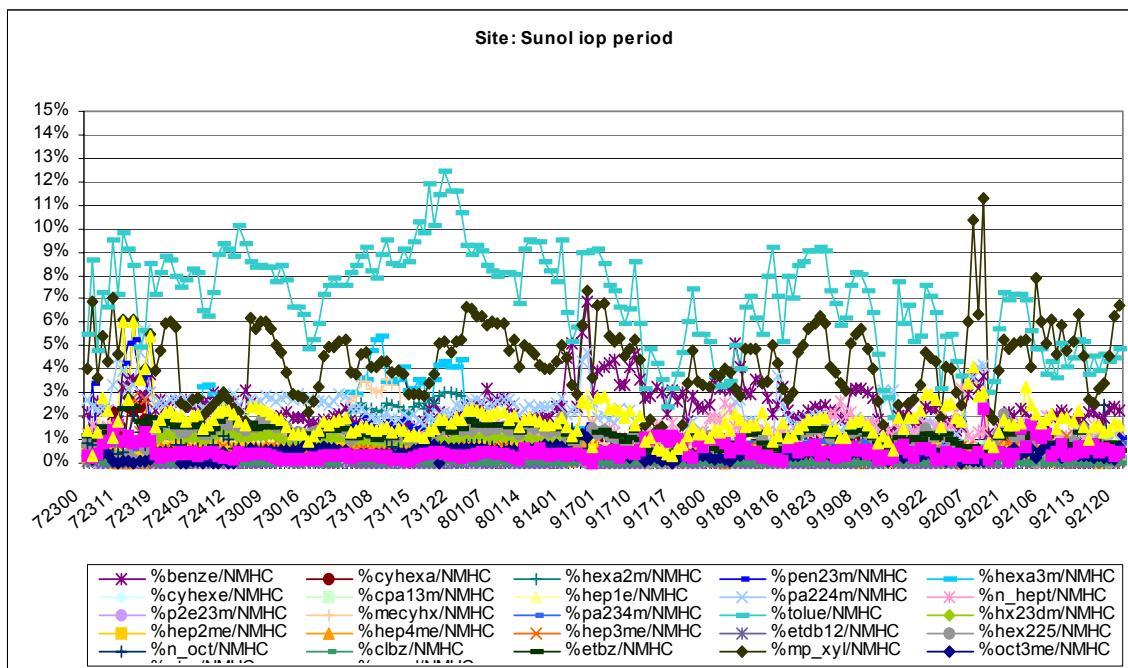
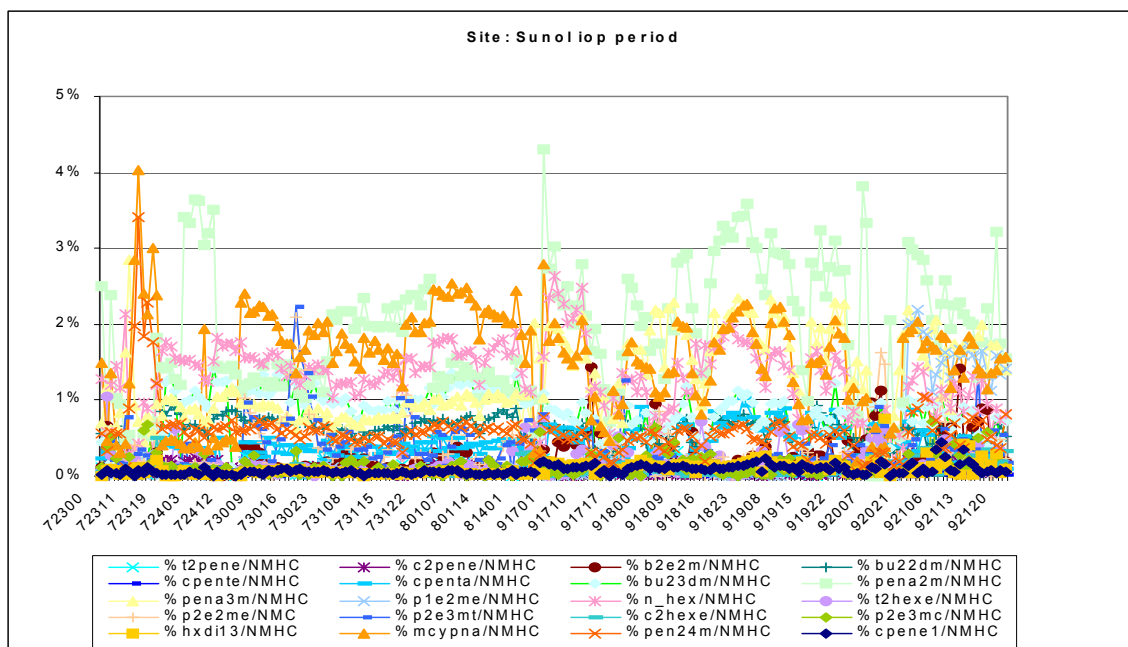
6.1 Appendix A: Time Series of Ambient Data for Granite Bay

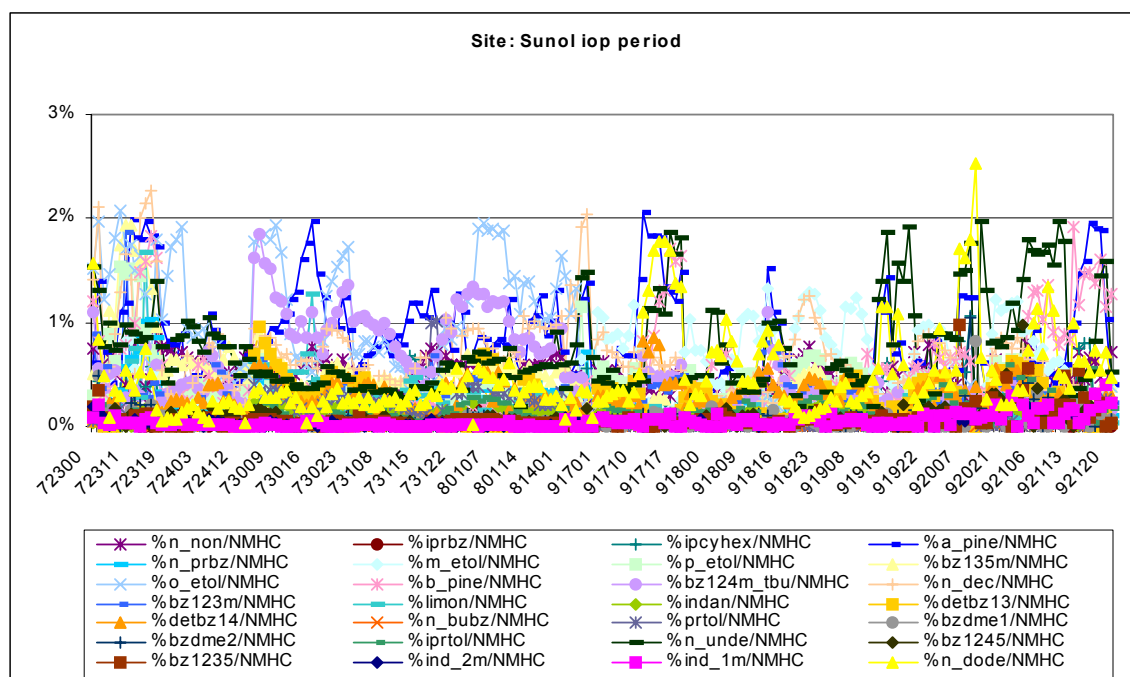




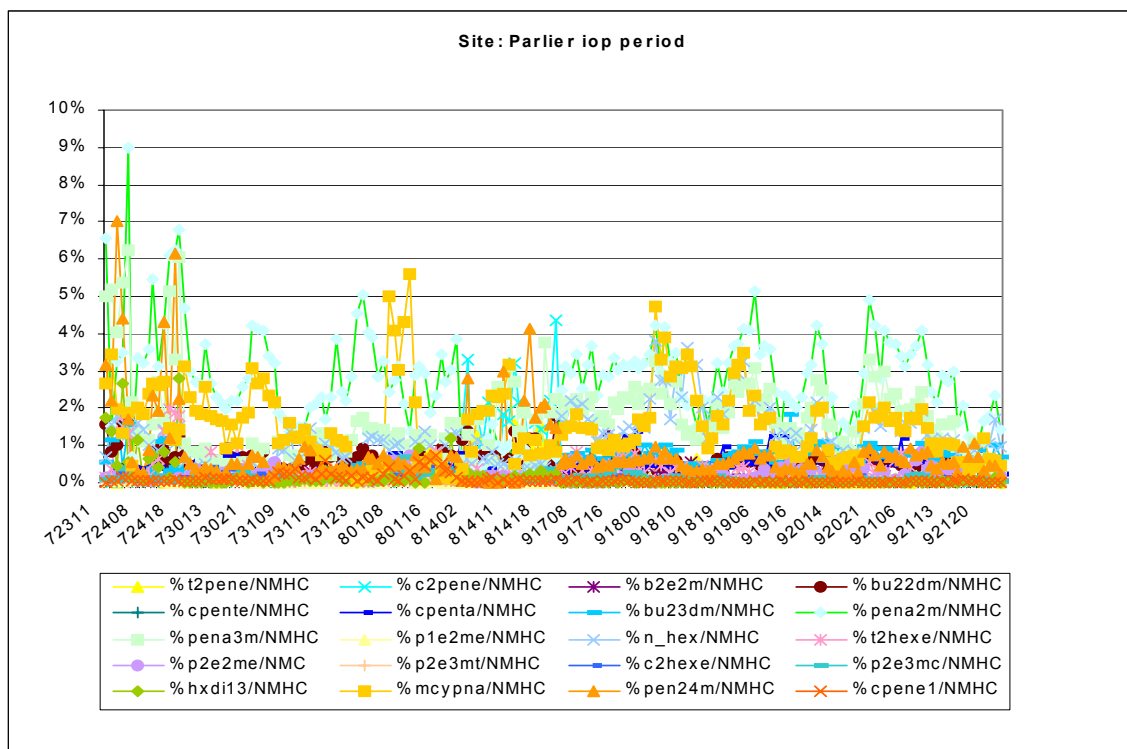
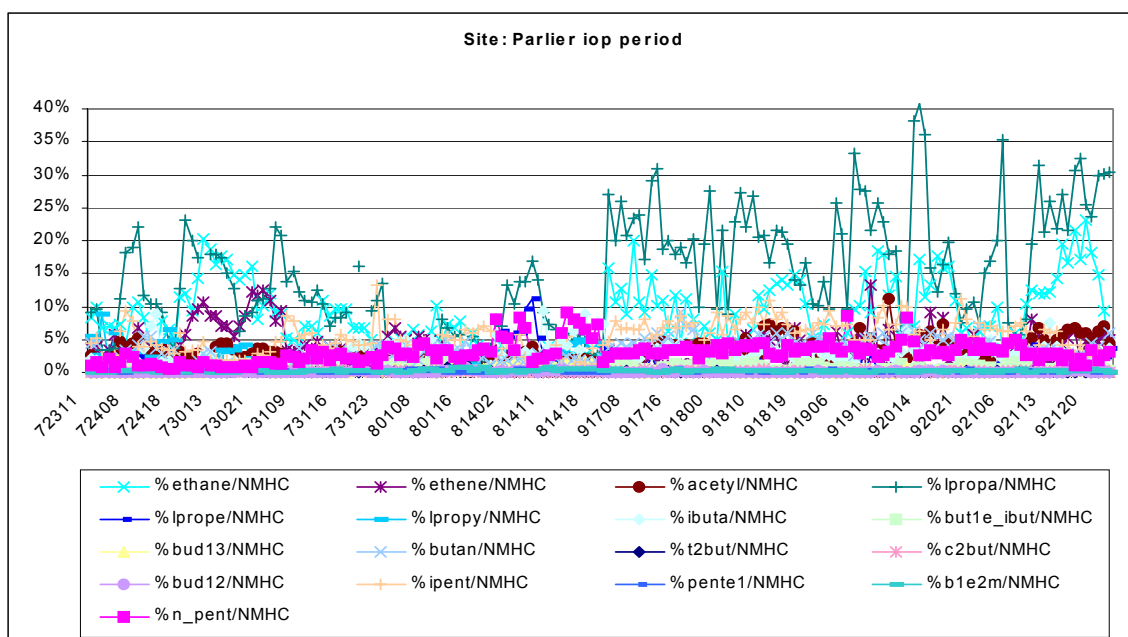
6.2 Appendix B: Time Series of Ambient Data for Sunol

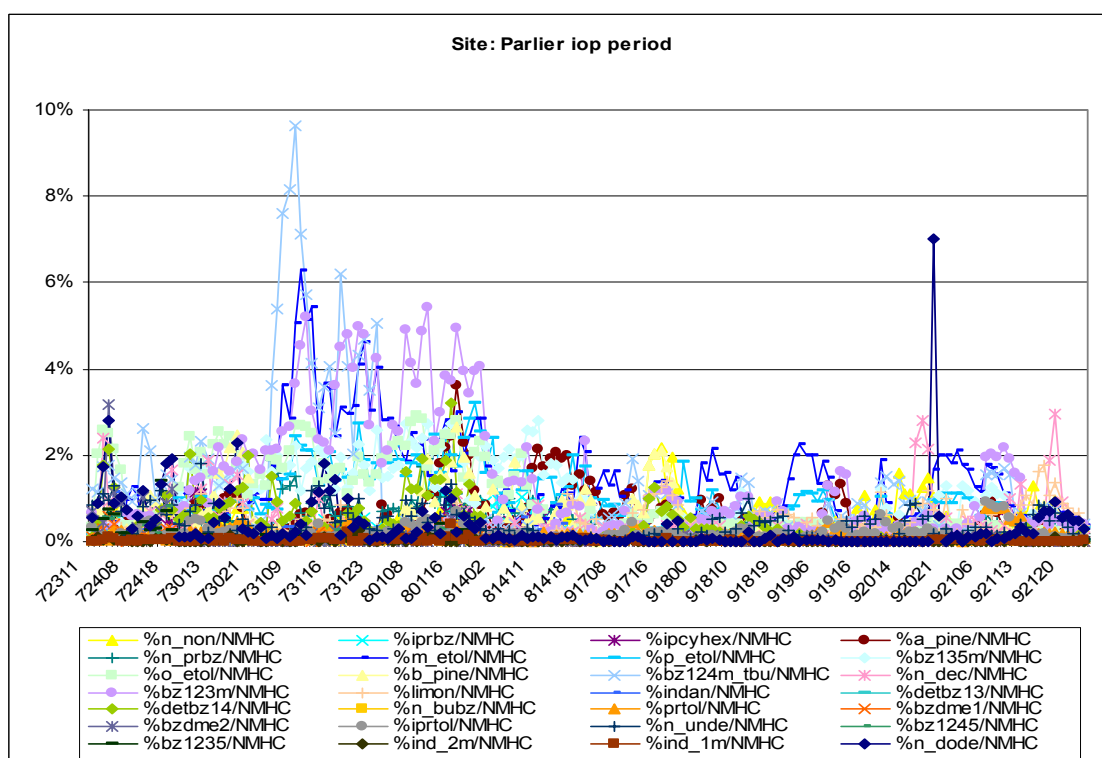
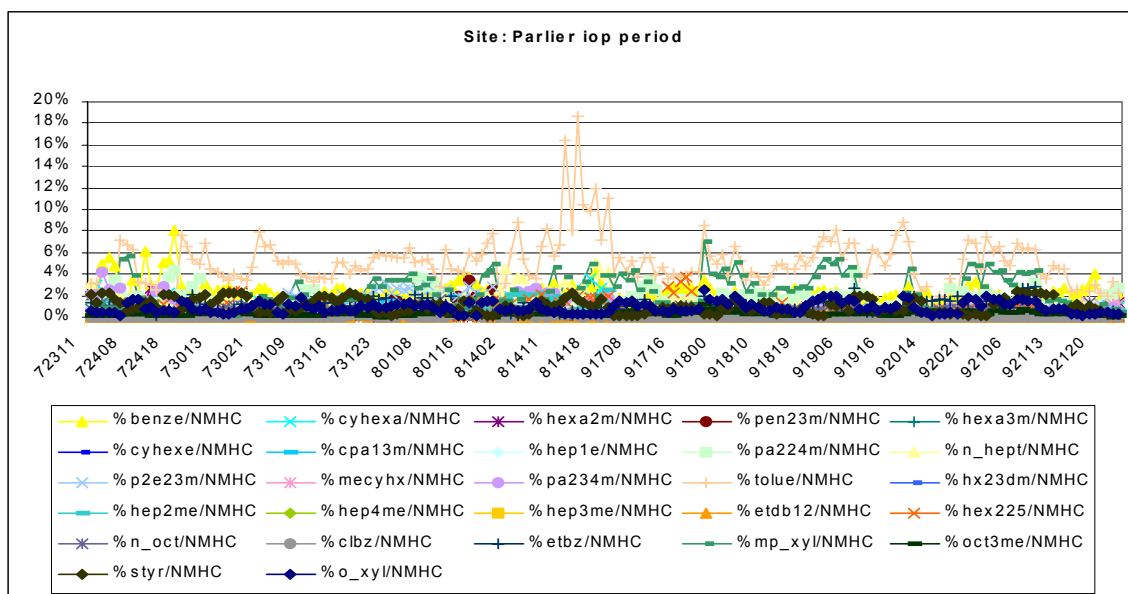






6.3 Appendix C: Time Series of Ambient Data for Parlier





6.4 Appendix D: Descriptive Statistics for Granite Bay

	Canister	GC/MS
No of values used	54	54
No of values ignored	0	0
No of min. val.	1	1
% of min. val.	1.852	1.852
Minimum	0.020	0.009
1st quartile	0.250	0.246
Median	0.580	0.493
3rd quartile	1.540	1.330
Maximum	5.610	9.189
Range	5.590	9.179
Total	60.930	61.185
Mean	1.128	1.133
Geometric mean	0.513	0.452
Harmonic mean	0.183	0.108
Kurtosis (Pearson)	2.843	8.917
Skewness (Pearson)	1.869	2.804
Kurtosis	3.489	10.420
Skewness	1.977	2.967
CV (standard deviation/mean)	1.241	1.476
Sample variance	1.924	2.746
Estimated variance	1.960	2.798
Sample standard deviation	1.387	1.657
Estimated standard deviation	1.400	1.673
Mean absolute deviation	1.001	1.060
Standard deviation of the mean	0.191	0.228

6.5 Appendix E: Descriptive Statistics for Sunol

	Canister	GC/MS
No of values used	54	54
No of values ignored	0	0
No of min. val.	1	1
% of min. val.	1.852	1.852
Minimum	0.010	0.010
1st quartile	0.270	0.277
Median	0.490	0.486
3rd quartile	1.110	1.699
Maximum	6.740	6.742
Range	6.730	6.732
Total	57.870	66.602
Mean	1.072	1.233
Geometric mean	0.501	0.582
Harmonic mean	0.173	0.192
Kurtosis (Pearson)	4.268	3.502
Skewness (Pearson)	2.149	2.000
Kurtosis	5.115	4.241
Skewness	2.274	2.116
CV (standard deviation/mean)	1.328	1.283
Sample variance	1.988	2.456
Estimated variance	2.026	2.503
Sample standard deviation	1.410	1.567
Estimated standard deviation	1.423	1.582
Mean absolute deviation	0.972	1.124
Standard deviation of the mean	0.194	0.215

6.6 Appendix F: Descriptive Statistics for Parlier

	Canister	GC/MS
No of values used	54	54
No of values ignored	0	0
No of min. val.	1	1
% of min. val.	1.852	1.852
Minimum	0.070	0.071
1st quartile	0.600	0.359
Median	1.585	1.290
3rd quartile	3.310	3.151
Maximum	41.000	39.428
Range	40.930	39.357
Total	191.278	183.209
Mean	3.542	3.393
Geometric mean	1.517	1.287
Harmonic mean	0.656	0.498
Kurtosis (Pearson)	19.735	19.632
Skewness (Pearson)	4.105	4.043
Kurtosis	22.764	22.647
Skewness	4.344	4.277
CV (standard deviation/mean)	1.804	1.810
Sample variance	40.086	36.994
Estimated variance	40.843	37.692
Sample standard deviation	6.331	6.082
Estimated standard deviation	6.391	6.139
Mean absolute deviation	3.469	3.479
Standard deviation of the mean	0.870	0.835